COPY NO. 15

TECHNICAL REPORT 4214

ELECTRIFICATION OF LEAD AZIDE POWDERS

UNDER AMBIENT CONDITIONS

BY

B. D. POLLOCK

W. B. ZIMNY

PICATINNY ARSENAL
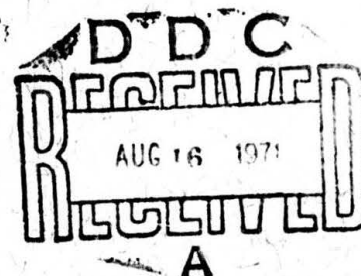
AND

C. R. WESTGATE

THE JOHNS HOPKINS UNIVERSITY

JUNE 1971

PICATINNY ARSENAL

DOVER, NEW JERSEY

DDC

RECEIVED

AUG 16 1971

A

DOCUMENT CONTROL DATA - R & D

(Security classification of title, body of abstract and indexing annotation must be entered when the overall report is classified)

1. ORIGINATING ACTIVITY (Corporate author)	2a. REPORT SECURITY CLASSIFICATION
Picatinny Arsenal, Dover, N. J.	UNCLASSIFIED
	2b. GROUP

3. REPORT TITLE

ELECTRIFICATION OF LEAD AZIDE POWDERS UNDER AMBIENT CONDITIONS

4. DESCRIPTIVE NOTES *(Type of report and inclusive dates)*

5. AUTHOR(S) *(First name, middle initial, last name)*

B. D. Pollock
W. B. Zimny

6. REPORT DATE	7a. TOTAL NO. OF PAGES	7b. NO. OF REFS
JUNE 1971	37	
8a. CONTRACT OR GRANT NO.	9a. ORIGINATOR'S REPORT NUMBER(S)	
b. PROJECT NO.	Technical Report 4214	
c.	9b. OTHER REPORT NO(S) *(Any other numbers that may be assigned this report)*	
d.		

10. DISTRIBUTION STATEMENT

Approved for public release; distribution unlimited.

11. SUPPLEMENTARY NOTES	12. SPONSORING MILITARY ACTIVITY

13. ABSTRACT   The electrification of lead azide powders was studied under ambient conditions by means of a vibrating trough apparatus. Five azides were studied: two were dextrinated types, two were RD 1333 types, and one was a polyvinyl alcohol (PVA) type. All were from commercial sources.

The experimental variables were: particle size; trough material; sample size, sample feed rate, and external electric field. The charge measured for a given weight followed very closely a square root dependence on weight in the range of sample weights used, and an inverse first power dependence on particle size in the 40 to 80 micron range of particle diameters. The inverse dependence on particle size corresponds to a constant surface charge concentration for a given powder. Applied fields of a few hundred volts per cm could neutralize the effect of spontaneous charging.

Differences between different lots or types of powder and between different metals were observed and are attributed in part to particle shape factors.

Reversals of charging sign were noted, usually associated with contact with stainless steel.

DD FORM **1473** REPLACES DD FORM 1473, 1 JAN 84, WHICH IS OBSOLETE FOR ARMY USE.

KEY WORDS	LINK A		LINK B		LINK C	
	ROLE	WT	ROLE	WT	ROLE	WT
Lead azide						
Electrification						
Contact charging						
Electrostatic hazards						
Electric field						
Non-conducting powders						

Technical Report 4214

ELECTRIFICATION OF LEAD AZIDE POWDERS
UNDER AMBIENT CONDITIONS

by

B. D. Pollock
W. B. Zimny

Picatinny   Arsenal

and

C. R. Westgate

The Johns Hopkins University

June 1971

ACKNOWLEDGMENTS

TABLE OF CONTENTS

Tables

Figures

ABSTRACT

The electrification of lead azide powders was studied under ambient conditions by means of a vibrating trough apparatus. Five azides were studied: two were dextrinated types, two were RD 1333 types, and one was a polyvinyl alcohol (PVA) type. All were from commercial sources.

The experimental variables were: particle size; trough material; sample size, sample feed rate, and external electric field. The charge measured for a given weight followed very closely a square root dependence on weight in the range of sample weights used, and an inverse first power dependence on particle size in the 40 to 80 micron range of particle diameters. The inverse dependence on particle size corresponds to a constant surface charge concentration for a given powder. Applied fields of a few hundred volts per cm could neutralize the effect of spontaneous charging.

Differences between different lots or types of powder and between different metals were observed and are attributed in part to particle shape factors.

Reversals of charging sign were noted, usually associated with contact with stainless steel.

1

INTRODUCTION

This work is part of a study to characterize the electrification behavior and charge relaxation processes of lead azide in contact with common metals and in particular to investigate the effect of water vapor and of CO_2 on such behavior. The work is a continuation of experiments by P. Mahler (Ref 1) on lead azide and of work by Avrami, Schwartz, and Levy (Ref 2) with inert powders. This report describes experiments conducted under ambient conditions.

Mahler carried out electrification experiments intended to simulate the electrification process in a Jones loader. In his experiments, he obtained limiting voltages as high as 860 volts. Although his results were qualitative, he did show that lead azide can be an effective medium for the generation of electric charges.

Avrami, Schwartz, and Levy used an apparatus consisting of a metal hopper fitted with adjustable orifices, a metal receiver, and an electrostatic voltmeter connected to the two containers. The latter were insulated and were mounted in a Faraday box. Using 500-600 gms of aluminum oxide in most of their experiments, they were able to generate charges of about 1×10^{-6} coulomb at limiting voltages estimated to have been as high as 7 - 9 Kv. They noted the effects of ball-milling, as well as the effects of particle size, orifice material, and humidity. They also observed large and usually unpredictable effects on charging that were attributed to electric fields resulting from charging of structural surfaces by dust, or by wiping parts of the apparatus with a cloth incidental to cleaning. In earlier work, Rathburg and Schmitz (Ref 3) carried out electrification experiments on several propellants, and primary and secondary explosives as part of an electrostatic hazards evaluation. Their approach was to measure voltages generated when 50-1000 gms of powder were poured from a drying rack into a metal-lined, insulated holding tray. The capacitance to ground of the tray and rack were known. They could therefore calculate the electrostatic energy generated during the pouring operation and compare the energies with those required to initiate the explosive under study in a spark discharge test. A number of observations that they made are of interest in this work.

Charging followed a less than linear function of quantity of explosive. Air flow did not generate any additional charge. Differences were observed between various rack-covering materials. In the 46-73% range, changes of relative humidity had little effect on charging. Ultraviolet radiation reduced the insulation resistance of the apparatus from 2×10^{13} to 5×10^{11} ohms, while radioactive sources equivalent to 4.5 mg of radium reduced the insulation resistance to 10^9 ohms in the most favorable case.

The line of thinking and the approach taken in the work reported here were considerably influenced by a paper (Ref 4) and a monograph (Ref 5) by Harper. He stresses the virtual impossibility of obtaining ideally pure, or atomically clean, surfaces and the practical difficulty in obtaining even reproducible "cleaned" surfaces. The term "cleaned" in this context refers to treatment intended to remove surface contamination. Different treatments may therefore leave surfaces with different electronic properties. One would expect common metals to have an oxide (or other reaction product) coating on which there would, under ambient conditions, be adsorbed an outer layer of water vapor or other gases. In the case of a reactive compound such as lead azide, one might reasonably expect to find a similar complex surface composition.

Two points discussed by Harper concern the nature of solid-solid contact. First, areas of such close contact that transfer of charge can occur are very small and represent a very small fraction of a given geometrical surface. One consequence of this fact is that it is possible for contact to occur on different kinds of surfaces due to variations in orientation, structural imperfections or other inhomogeneities. Second, reference is made to "smooth" versus "adherent" sliding. The distinction of importance in this work is that, when sliding occurs, it is possible for effective surface compositions to be changed, and thus the charging process may be affected.

Harper also made a distinction between the electrical (or electronic) characteristics of metal-metal and metal-semiconductor contacts. In the case of metal-metal contacts, he postulates that, as the metals approach and the separation reaches a critical gap thickness, electrons pass between the metals by tunneling across the gap and redistributing themselves virtually instantaneously, and the charge is on the surface. This he calls "separation charging". In

3

the case of metal-semiconductor contact in which the semiconductor has a fairly high resistivity, charge transfer would require essentially direct or mechanical contact, the distribution of the charge would require appreciable time, and the charge layer would be of some finite real thickness. This situation he calls "contact charging".

Since lead azide is highly insulating, this material would be expected to charge according to the contact model. The use of a method based on powder as the sample form, and vibration or fall of powder lends itself not only to the study of the extent of charging but also of charging dynamics. When such a technique is used the important experimental variables are time and number of contacts, particle size, and nature or composition of contacting surfaces. The latter are conveniently investigated by use of different materials and atmosphers. Thus the method offers the advantages of mechanical simplicity and avoids problems incident to the preparation of special shapes or forms of sample. Further, by the use of sensitive instruments in low capacity measuring circuits it is possible to use very small quantities of explosive. These two factors are of concern for laboratory safety reasons. And finally, results would be fairly directly and uambiguously applied to lead azide in its usual technologically important form.

EXPERIMENTAL

Materials

All the lead azides used in the electrification work were commercial materials which were prepared by addition of aqueous sodium azide to solutions of lead acetate or nitrate containing additives whose function was to control particle size and shape. Dextrinated lead azide was precipitated in the presence of dextrin and contains approximately 98% PbN_6. RD 1333 is precipitated in the presence of sodium carboxymethyl cellulose and contains about 98.5% PbN_6. The PVA lead azide is precipitated in the presence of polyvinyl alcohol (PVA) and contains about 98% PbN_6.

These explosives are normally stored and shipped under 50/50 water/ethyl alcohol mixtures. For this work, sufficient amounts of each representative lot were removed, dried, and divided into 5-gram

4

portions which were put in conductive rubber bottles. These small batches were used for the laboratory experiments.

For particle size experiments, 1/2 - 1 gm portions were sieved in an Allen-Bradley "Sonic Sifter", and each size-fraction was put into small polyethylene vials labelled by lot number and size range. The sieves had openings ranging in sizes from 37 through 88 microns, in increment ratios of approximately 18%. It was found that sieving tends to break up the agglomerates and thereby to give increased fractions of fines. Since it was desired to obtain as much material as possible of narrowly defined sizes, sieving was usually limited to 1 - 2 minutes.

The powders were characterized by size distribution and by microscopic appearance. The particle size distributions were log normal, as shown by linear plots of cumulative size fractions on log normal probability paper. Results of the screen analyses, together with brief notes on appearance, are summarized in Table 1 in terms of the particle size parameters M', and ρg. The quantity M' is the weight-median, or "50%" diameter and ρ_g is the geometric standard deviation given by the ratio of the "83.14% diameter" to the weight-median value. The notation is that used by Orr and Dallavale (Ref 10), and the values in the table were taken from plots on log normal probability paper.

TABLE 1

Data on lead azide powders

Powder by lot and type	Sieve Analysis M' (in microns)	ρg	Microscopic Appearance
OMC 2-2 RD 1333	64	1.22	Rough sharp-edged pebble-like crystallites or clusters
OMC 69-104 dextrinated	47	1.22	Rounded clusters
OMC 69-1 PVA	48	1.25	Clusters of a few rod-like small crystals
Dup 51-49 RD 1333	49	1.61	"Holly leaf" outline, with many points.
Dup 52-238 dexrinated	32	1.44	Aggregates of many small crystallites about 15-25 microns on edge

Photograpsh of the 53 - 63 micron size fraction are shown in Figures 1a through 1e.

Apparatus

The apparatus is shown schematically in Figure 2. Its essential parts consisted of a metal trough driven by a Syntron model F-TO 15-watt vibratory feeder, and a Faraday cage containing a small aluminum planchet connected to a Keithley Model 610B or 640 electrometer operated in the coulomb mode. Three troughs were used. They were 8" lengths of 1/4" x 1/2" aluminum, stainless steel, or gold-plated brass. Each had a rectangular groove, 3/16" deep and 3/8" wide, milled for 7" of its length. The troughs were clamped by a pair of Teflon bridges, to a Lucite plate which in turn was screwed to the driven member of the vibratory feeder. The bridges were machined so that they could support a 1/8" diameter brass rod

6

electrode above the grooves for experiments with electric fields.
As assembled, these parts were insulated from the chassis or vibrator but in all experiments not using applied electric fields, all parts were grounded to a common chassis plate or the rod was replaced by an aluminum foil cover over the trough, in order to shield the powder from the effects of extraneous fields.

Procedures

In preliminary experiments with red lead oxide, it was found that wiping the troughs with solvents such as trichlorethylene or acetone did not give reproducible results in successive experiments. It was not considered feasible to prepare the surfaces of the troughs by outgassing in vacuum at elevated temperatures, as was done by Debeau (Ref 6) and Wagner (Ref 7), especially since the azide could not be given an equivalent treatment. Therefore, to obtain reproducibility, the troughs were "conditioned"-rather than being cleaned by vibrating a few preliminary batches of the given test powder until results stabilized. Usually 2-4 portions of about 10 mgs were sufficient. It is postulated that the first few batches wiped off residues from previous experiments and leaves its own residue, the composition of which is fairly constant. It may be recalled from the Introduction that adherent sliding might cause changes in surface composition. For this reason, each test sample was used only once and was then disposed of in a ceric ammonium nitrate kill solution. Although, in plant operations, azide may be recycled, it was believed desirable not to reuse powders in this work, to keep experimental variables at a minimum.

A charge measurement was made as follows: in the case of as-received (unsized) azide, about 1/4 - 1/2 gm of azide was transferred from the laboratory container to a conductive rubber dispensing cup by means of a plastic spoon. If "sized" powder was being used, the plastic vial containing a given size fraction was put in a small brass holder to avoid spilling and to provide safety in handling.

Small increments, ranging from fractional mg to 35 mgs, estimated visually, were then put into the end of the trough with a small plastic measuring spoon. The zero adjustment on the instrument was checked, and then the "zero check" button of the electrometer released and the switch of the vibrator power supply turned on simultaneously. The meter needle remained stationary until powder began

falling into the Faraday cup. When all the powder was completely vibrated off the trough, the corresponding deflection of the meter was noted, the vibration was stopped, the "zero check" button of the electrometer was returned to the "lock" position, and the weight of the powder on the aluminum planchet was determined.

In a number of supplementary tests, it was found that charges measured for a given mass of powder were not sensitive to the vibrator power setting as long as all the powder was transferred to the cup. The vibrator setting for most of this work was therefore at 70% of maximum, estimated to correspond to about 12 watts input power. This setting was taken as being a good compromise that would give a high degree of contacting consistent with complete transfer of powder. At this setting, transfer of powder took 4-6 seconds if the powder was put into the trough in a batch. If the powder was allowed to trickle slowly into the end of the trough, it took a given particle about 2-3 seconds to traverse the length of the trough.

It was also found that charging does not seem to be sensitive to the length of the flow path. Thus the amount of charge did not decrease noticeably until the powder was put on the trough within 1 - 1 1/2 inch of the end. Apparently, charging to saturation occurs fairly rapidly. Any initial charge placed on the powder as a result of handling, such as contact with the plastic transfer spoon or the small glass beaker sometimes used to weigh samples, was observed to be very quickly erased.

RESULTS

Sign of Charging; Sign Reversal

The unsieved powders were found to charge negatively against aluminum and gold, and positively against stainless steel. When experiments with sieved powders began, however, this behavior was not followed consistently. Two sets of experiments illustrate the inconsistency sometimes noted.

In the first particle-size effect experiments with Dup 51-49, the fractions smaller than 88 microns charged positively, while the fraction larger than 88 microns charged negatively in the aluminum trough.

8

It should be noted that the sieves having openings of 88 microns and larger are made with brass screens, and those having openings 73 through 37 microns are made with stainless steel screens.

In a later set of experiments to check on the extent and repeatability of the sign changing effect, the Dup 51-49 did not behave as above. In this set of experiments, the procedure was to put 0.1 - 0.2 gm of a given powder on the top sieve of a stack consisting of the 88, 73, and 37 micron sieves, and then to carry out the size fractionation as for a size-effect experiment. A few mgs of the fraction on the 88 micron sieve were then tested in duplicate in the aluminum trough. A few mgs of the fractions on the 37 and 73 micron sieves were tested in a similar manner. All of the other azide powders were also tested. In this set of experiments, only the smaller-than-88 micron fraction of the OMC 69-1 charged positively. All other fractions of all the powders charged negatively.

Such changes in charging sign occurred in later experiments, usually associated with contact with stainless steel at some stage. When these changes did occur, the sign of charge persisted, and charging behavior and magnitude of charging were similar to those of the negatively charging powders.

Charging Curves and Difference in Lots

In most of these experiments, the "charging curves" (or plots of charge vs weight of sample) were obtained by putting the powder into the end of the trough before turning the vibrator on. In these experiments, the charging was found to be nonlinear with sample weight and, in the 1 - 35 mg range, it followed very closely a square root dependence on quantity:

$$q = Km^{1/2} \tag{1}$$

This behavior is shown in the log-log plots of Figures 3 and 4. The nonlinear behavior is due to particle-particle interaction, which is discussed in a later section of this report.

The charges on 10 mg of the lots studied here are given in column 2 of Table 2 and the value for OMC 2-2 was taken from Table 3. The other values were taken from the plots of Figure 3. The data are for unsized powder.

9

TABLE 2

Charging of azides on aluminum

Lot (and type)	Charge in coulombs on 10 mg	Charge density (coul/cm^2)
OMC 2-2 (RD 1333)	2.8×10^{-11}	8.2×10^{-12}
OMC 69 104 (dex)	7.4×10^{-11}	16.1×10^{-12}
OMC 69-1 (PVA)	2.2×10^{-11}	4.8×10^{-12}
Dup 51-49 (RD 1333)	5.8×10^{-11}	19.3×10^{-12}
Dup 52-238 (dex)	4.7×10^{-11}	5.7×10^{-12}

The charge densities, Q/A, in the third column were calculated using the particle size parameter data in Table 1, as an estimated effective particle density of 3.0 gm/cc, and Equation 2 from the reference on particle measurement by Orr and Dallavalle (Ref 10):

$$\text{Log } d_s = \text{Log } M' - 4.605 \, (\text{Log } \rho_g)^2 . \qquad (2)$$

Here d_s is the surface mean particle diameter, and the value for M' and ρg are then given in Table 1.

In making a comparison of the values in the third column, it might be noted that later in these "Results" it is shown than in a given powder, the charge density, in the coulombs/cm^2 of particle surface, is independent of particle diameter. Thus the charge density, Q/A at a given sample weight is a measure of the charging capacity of powders independent of particle size distribution. Because of some uncertainties in the shape factor or effective densities, only qualitative comparison between the lots can be made, although the low results of OMC 69-1 undoubtedly reflects the particle shape.

In a later experiment, particle-particle interaction was eliminated, or largely reduced, by allowing the powder to trickle very slowly at an even rate into the trough while the latter was in vibration. It was found that at feed rates of 0.1 to 0.2 mg/sec the charge was linear with quantity, and charging per unit mass was at maximum. Charging by this procedure is compared with charging by the "batch" procedure in Table 4, in connection with a study of the size effect.

Effect of Trough Material

The influence of trough material on charging was investigated by observing the magnitude and sign of charge on two different types of azide in contact with aluminum, gold, and stainless steel. One of the azides was a dextrinated grade, OMC 69-104, and the other was an RD 1333 grade, OMC 2-2.

The results are summarized in Table 3. The values are averages of five or six samples, except that, for the experiment with OMC 2-2 in gold, only one sample could be run. The values in parentheses are the standard deviations.

The data illustrates the usual charging signs; i.e., the aluminum and gold give rise to negative charges, and the stainless steel gives the positive charge in both azides. In addition, it may be seen that, for all metals, the OMC 2-2 charges more positively (or alternately, less negatively) than the OMC 69-104. A third point is that, for both azides, charging is in the direction of increasing positive charge, in the order aluminum, gold, stainless steel.

Effect of Applied Electric Field on Charging

Two groups of experiments were performed with OMC 2-2 azide in the stainless steel trough. Because of the circular cross section of the electrode, the rectangular dimensions of the trough and the fact that the powder spread nonuniformly across the trough, it was not possible to calculate an unambiguous field strength. However it is estimated that the field strength did not vary over a factor of two across the bottom of the trough.

The first experiments were performed with a limited amount of powder of 37 - 44 micron particle diameter. Data were taken with applied voltages of 0, +200, and +300 volts only. The corresponding electrometer readings were +3.70, +1.15, and +0.36 volts, respectively. By extrapolation to zero charge, +330 volts (applied across a nominal 1/8 inch gap) was found to be required to just compensate for contact charging.

The second set of data was taken with powders ranging in particle size from 37 to 73 microns, or a nominal mean of 55 microns.

11

TABLE 3

Charge vs trough material

Charge in Coulombs on 10 mg

Powder	Aluminum	Gold	Stainless Steel
OMC 69-104 (dext)	$-4.14 \, (.24) \times 10^{-11}$	$-1.41 \, (.05) \times 10^{-11}$	$+0.52 \, (.04) \times 10^{-11}$
OMC 2-2 (RD1333)	$-2.83 \, (.12) \times 10^{-11}$	$-0.41 \, (---) \times 10^{-11}$	$+1.24 \, (.09) \times 10^{-11}$

12

The data is summarized in the curve of Figure 6 which shows that an applied voltage of +220 would be required to compensate for contact charging for particles of this size. These results show that lower compensating fields are required for larger particles, in qualitative agreement with theoretical considerations. (Refer to Appendix C.)

The plot also shows linearity in the range +400 to -400 volts. Beyond about +400 volts the curve shows a minimum and beyond -400 volts it shows evidence of a maximum. This behavior is due to charge transfer between the particles and the upper electrode that occurs when the particles are picked up due to electrostatic attraction. The effect was also shown very clearly in earlier experiments with lead oxide. It is not considered significant to this work.

Effect of Particle Size

The effect of particle size on charging was investigated in four experiments. In the first, Dup 51-49 powder was used in the aluminum trough. In the second and third, OMC 2-2 was used in aluminum and stainless steel, respectively. In these first three experiments, the procedure was to put the powder in the end of the trough in a batch. The results were therefore influenced by particle-particle interaction. To determine whether effects that had been considered due to particle size were actually due to particle-particle interaction, the fourth experiment was run using the "trickle feed" procedure described earlier under "Charging Curves". This procedure results in a linear dependence of charge on amount of powder and is considered to be free of particle interactions.

Results of the experiments are summarized in Table 4. The arithmetic mean diameters of the given size fractions are listed in the first column under "Particle Diameters" and the corresponding ranges of particle size are shown in parentheses. Measured charges are given in the second, fourth, and sixth columns. The data for the fourth experiment, which was derived from the plots of Figure 5 is given in column six in parentheses, below that for the third run. Inspection of the data for charge vs particle size shows clearly that the charge decreases with increasing particle size.

To investigate the functional dependence of the charge on particle size, the charge per unit area of particle surface was calculated for each size fraction according to Equation 3, the derivation of which

13

is given in Appendix A. Equation 3 states that

$$Q/A = \frac{Q_i \, R_i \, \rho}{3m} \tag{3}$$

where Q/A is the charge density in coulombs per cm^2, Q_i is the measured charge on the "ith" fraction, R_i is the aritmetic mean radius, (i.e., one half of the diameter listed in the first column of Table 4). ρ is the effective particle density, and m is the sample weight. Results of the calculations are given in columns three, five and seven. It may be seen that the surface charge concentration Q/A is independent of particle size.

DISCUSSION

The work described above has shown that the charging of lead azide is dependent on particle size, lot or type of powder, materials of contact, quantity and feed rate, and on external field. A number of these which are of importance technologically in connection with the generation of an electrostatic hazard, will be briefly discussed first.

It is apparent from an examination of the data on charging in Table 2 that different lots and types of azide vary appreciably in their capacity to be charged. If the powders examined in this work are considered to be representative of those encountered in practice, one may estimate that the range of "chargeability" may be in the ratio of 5 or 10 to 1. A second point is that charging is influenced by the materials of construction. Thus of the two common metals used here, the stainless steel gave rise to the lesser charging and the charge tended to be positive. Such materials may be used to minimize charge generation.

The results of the applied electric field experiments have some important practical implications. It is apparent that such fields are probably much more important in practice in the generation of charge than is the contact charging. From a hazards point of view it would be profitable to monitor extraneous fields to which the azides (and presumably, any other non-conductive explosives), are subjected during handling.

14

TABLE 4

Charge vs particle size

Particle Diameters in microns	Dap 51-49 in Aluminum Trough		OMC 2-2 in Aluminum Trough		OMC 2-2 in Stainless Steel Trough	
	Coulombs for 5 mgs ($\times 10^{-11}$)	Coulombs per cm² ($\times 10^{-12}$)	Coulombs for 5 mgs ($\times 10^{-11}$)	Coulombs per cm²	Coulombs for 10 mgs	Coulombs per cm² ($\times 10^{-12}$)
40 (37-44)	+2.7	10.8				
48 (44-53)	+2.1	10.1	-1.79	8.6×10^{-11}	$+7.4 \times 10^{-11}$ $+(30.4 \times 10^{-11})$	14.8 (60.8)
58 (53-63)			-.47	8.5×10^{-12}	$+6.6 \times 10^{-11}$ $+(20.0 \times 10^{-11})$	19.2 (58.0)
68 (63-74)	+1.6	10.9	-1.19	8.3×10^{-12}	$+5.0 \times 10^{-11}$ $+(18.8 \times 10^{-11})$	17.5 (68.0)
81 (74-88)			-1.05	8.4×10^{-12}	$+4.0 \times 10^{-11}$ $+(14.0 \times 10^{-14})$	16.0 (57.4)
Average	+10.6		-8.5×10^{-12}		+16.9 +(63.0)	

The electric field experiments also suggest the feasibility of using controlled electric fields to minimize the generation of electrostatic energy as a novel means of reducing hazards. It should be noted that the fields can be used to neutralize effects of spontaneous charging. This neutralization is due to an induction effect that does not require that the power supply provide continuous power. It is sufficient that an electrode having a low capacity to the trough (or other form of powder-handling system) be supplied by a voltage source which should have a high internal impedance. Under these conditions the energy stored in the electrode system would be low and, by virtue of the generally low fields required to effect neutralization, there would be little probability of sparking. Finally because of low electrode capacity and the need for a power supply of negligible power capability, there would be little shock hazard to personnel. In view of these factors, it seems quite safe to use controlled electric fields as a means of preventing the generation of electrostatic charges in sensitive areas. The feasibility of the idea depends, however, on being able to devise a charge-sensing electrode at a point below the exit point of powder from the trough, and to use the resulting signal to control a variable voltage, reversible polarity voltage source.

Now consider the nonlinear form of the charging curves. The nonlinear dependence is due to particle-particle interaction. The interaction is not due to decreasing the number of particle-to-metal contacts along the trough. Measurements made at different lengths from the end showed no significant differences. Rather, the effect of particle interaction is to inhibit charging of particles by modifying the electric field configuration in the vicinity of the particle contacts with the metal and with other particles.

Now consider the particle size experiments. These are significant in providing a test of the applicability of Harper's model (Ch. 12 Ref 5). Briefly, it is postulated that, in the case of a semiconductor or high resistance particle, the contact area becomes charged first in a primary charging process, and the rest of the particle then charges according to the equation

$$q = C V_{cp} (1 - e^{-t/rC})$$ (4)

where q is the charge on the particle, C is the capacity of the particle with respect to the metal surface, V_{cp} is the contact potential, t the contact time, r is the charging resistance, and rC is the time constant. After a sufficient time,

$$q_o = C V_{cp}$$

$$= R(0.5772 + 1/2 \ln(2R/Z_c)) V_{cp}. \quad (5)$$

R is the particle radius and Z_c is the separation between the particle and the metal. For a sample of mass M and effective density ρ the total charge Q is

$$Q = q_o N = R(0.5772 + 1/2 \ln(2R/Z_c)) V_{cp} \frac{M}{4/3 \pi R^3 \rho} \quad (6)$$

For a given mass of powder, the measured charge should be approximately proportional to $1/R^2$, and it can be shown that the charge per cm^2 of particle surface should be proportional to $1/R$.

The data given in Table 4 however shows that the charge for a given mass varies only as about $1/R$, and that the surface charge density is independent of R. It is possible that the discrepancy between the observed results and those predicted by Harper's model may be due to a large resistance and therefore too high a time constant. If such were the case, the primary charging process would predominate and results would then depend on the area of contact.

It is possible to make an order of magnitude estimate of the lower limit of the charging (and discharging) resistance of the particles based on the following considerations: In the vibrator, the trough is pulsed at the rate of 60 times per second in such a manner that the powder is made to move down it in a hopping manner. It is assumed that the particles make contact with the metal in a random way, but that all the available points of contact do touch metal, and become fully charged. If this were not true, one would not find the relative insensitivity to length of travel that was in fact observed. It is assumed also that the time of each contact is of the order of 1/120 second. If the time constant for charge migration were much less than this, the particles should reach or closely approach the limiting

17

charge given by Equation 5 during each contact, and the measured charge should depend on only the last contact. It may be recalled here that in the supplemental experiments mentioned in the "Experimental" section, charging did decrease when the length of travel became less than about 1 1/2 inch. At the setting of the vibrator power supply used in most of this work, it would take about 1 second for a particle to reach the end, and would entail 10 - 100 contacts. These facts indicate that the time constant must be very much larger than 1/120 second and is probably greater than 1 second. The capacity of the particles used in the particle size experiments are estimated to be in the order $1 - 2 \times 10^{-14}$ farad (see Appendix B). If the time constant is taken to be about 1 second, then the particle resistance for charging must be of the order of 10^{14} ohms.

The purpose of the above discussion is to demonstrate that in the time scale of these experiments, charge migration cannot be significant and that observed charge is primarily dependent on the extent of contact, i.e., on the first step in Harper's model, and by the discharge that occurs when contact is broken. Under these conditions, it is possible to explain the differences in charge densities in Table 2 and the effect of trough material illustrated in Table 3 in terms of particle shape factors such as number of points of contact per particle, the shape of the points and the surface finish of the metal. In this connection it should be pointed out that the particle size areas referred to in previous discussions of surface charge densities are the areas of imaginary spheres which circumscribe a particle of a given particle size. These geometric areas are used here as a measure of the extent of contact. Valid comparisons using surface charge densities based on these geometric areas can be made only if the amount of contact is proportional to the calculated area. This would be true when comparing different particle size fractions of a given lot. In that case, it is reasonable to assume that the number of contact points would be proportional to the geometric area and that the area of contact per point would be the same from size fraction to size fraction. This assumption is not warranted, however, when comparisons are being made between different lots. It is reasonable to assume that differences between lots are a reflection of different particle shapes or geometries if the residual charge is limited by discharge through the ambient gas(p200 Ref 5). Residual charge limitation is found in good insulators such as lead azide appears to be. With these factors in mind it may be noted that the range of surface charge densities given in the third column of Table 2, is about 3 1/2 to 1,

18

i.e., 4.8 - 16.1 x 10^{-12} coulombs/cm^2. Such a range seems very reasonable if particle shape factors are important in determining amount of contact and therefore important for charging.

One consequence of the limitation on residual charge due to gas discharge is that charge must be a function of gas pressure. Debeau observed a broad minimum in the range of pressure from about 0.1 - 1.0 mm Hg, in the charging of NaCl and quartz in air, oxygen, and nitrogen (Ref 6) and Medley also observed changes in charging with pressure (Ref 9).

Medley's experiments are also of interest in connection with the charge reversal noted earlier. In his experiments he used mercury which was caused to contact the lower surface of thin films of dielectric material. The top surfaces of the films were grounded through a mercury pool and an electrometer. The capacity of the film could be varied by changing its thickness, and the cell could be evacuated. Although the experiment was superficially different from the vibration of powders, it was similar in that Medley's configuration corre- to the contact between metal and a good insulator. He observed mea- sured charges that increased with increase in capacity of the film. His efforts, however, to obtain lower charge densities at a given film thickness by alloying the mercury with other metals, such as sodium or tin, resulted only in a reversal of sign of charge at the same charge density. Attempts to find a critical alloy composition gave indeterm- inate behavior of the instrument, and the sign reversal required only about 0.1% of alloying metal.

Behavior observed in this work is in qualitative agreement with that of Medley with respect to sign reversal, in that the magnitudes of charges were not markedly different when sign reversal occurred. Medley's explanation of the equality of charge with sign reversal is that the initial charge separation occuring on contact is very much greater than the residual charge that is actually measured. This would, however, imply a very sensitive dependence of charge sign on surface properties. Although the sign reversal is not well ex- plained, it is believed that the validity of the other results is not thereby impaired.

CONCLUSIONS

It is possible to make a number of definite conclusions concerning the charging of azide powders flowing in metal troughs:

1. Differences have been found in the charging of different azides. Although such differences are statistically significant, the range of charging, in terms of charge for a given mass and particle size, is about one order of magnitude.

2. Particle size experiments show that charging is proportional to particle surface area per unit mass. This implies that the electrification, i.e., charge transfer occurs at the points of intimate contact. Secondary charging (the charging of a particle's geometrical capacitance) was not important in our measurements because the times during which the particles were in contact with the troughs were too short.

3. External fields strongly affect charging and may have the potential to be used as an electrification control method.

4. Particle-particle interactions during flowing of powders are important in limiting charge accumulation, and charging is a maximum when particles are relatively isolated from each other during flow. Particle-particle interactions do not in any fundamental way affect the geometrical dependences of the transferred charge.

REFERENCES

1. P. Mahler, Unpublished work performed at P. A. in 1966

2. L. Avrami, F. R. Schwartz and P. W. Levy "The Buildup of Electrostatic Charges by Falling Powders. A Preliminary Report", PATR 3853, May 1969

3. Hans Rathsburg and L. Schmitz "Chemie-Enginieur Technik" 21 No.1 9/20 386-9 (1949)

4. W. R. Harper "How Do Solid Surfaces Become Charged" Paper No. 1, Procedings of the Static Electrification Conference, 1967, London

5. W. R. Harper "Contact and Frictional Electrification" Clarendon Press, Oxford 1967

6. D. E. DeBeau, Phys Rev 66 9-16 (1944)

7. P. E. Wagner J. Appl. Phys 25 501, 1954
            J. Appl. Phys 25 907, 1954

8. G. Haberman, Explosives Lab, FRL, unpublished data

9. J. A. Medley Brit. Jour. Applied Phys Suppl. No. 2, S28-30 (1953)

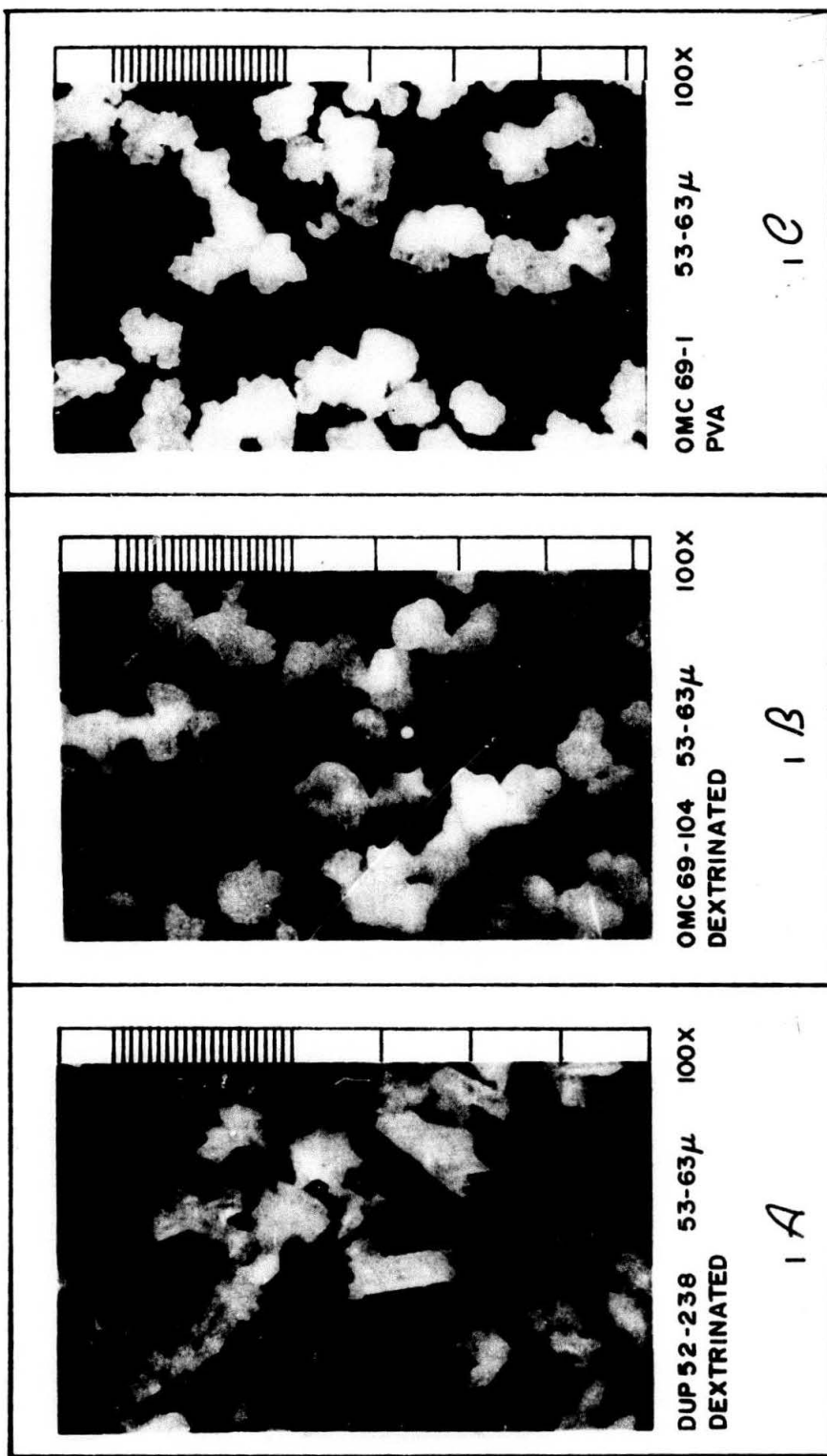10. C. Orr and J. M. Dallavalled "Fine Particle Measurement" pp 32-42 The Macmillan Co., N. Y. (1959)

Fig 1   Photomicrographs of five different lead azide powders at 100X;
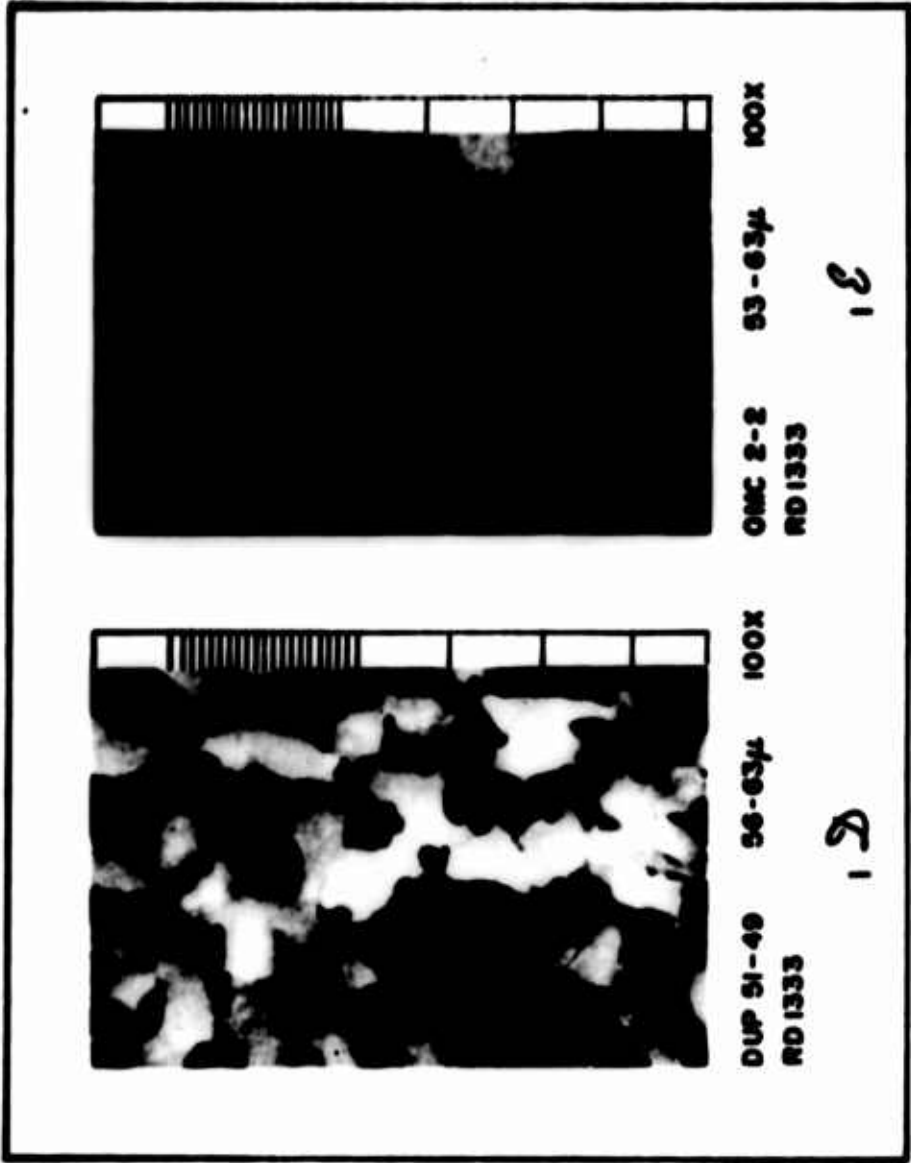Size from 53 - 63 μ, scale marks ~ 10 and 100 μ

Fig 1 (Cont'd) Photomicrographs of five different lead azide powders at 100X: Size from 53-63 μ, scale marks ~10 and 100 μ
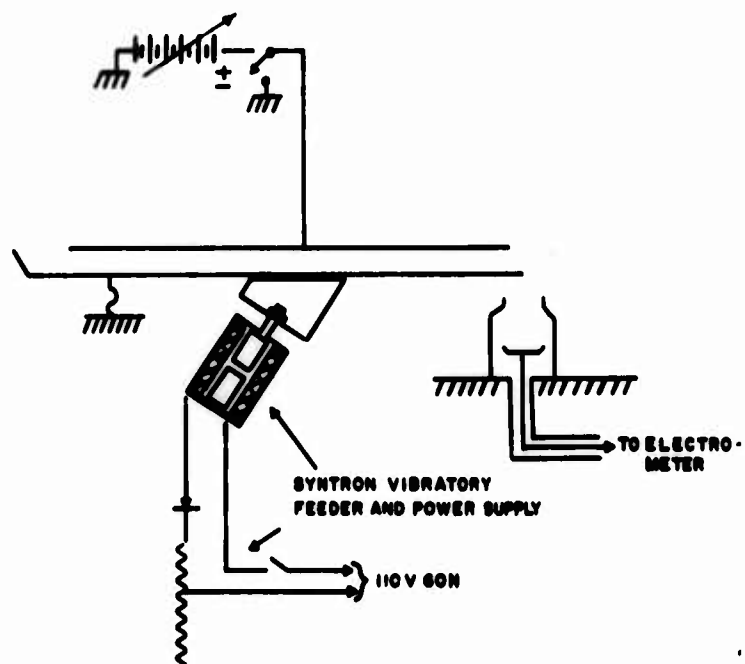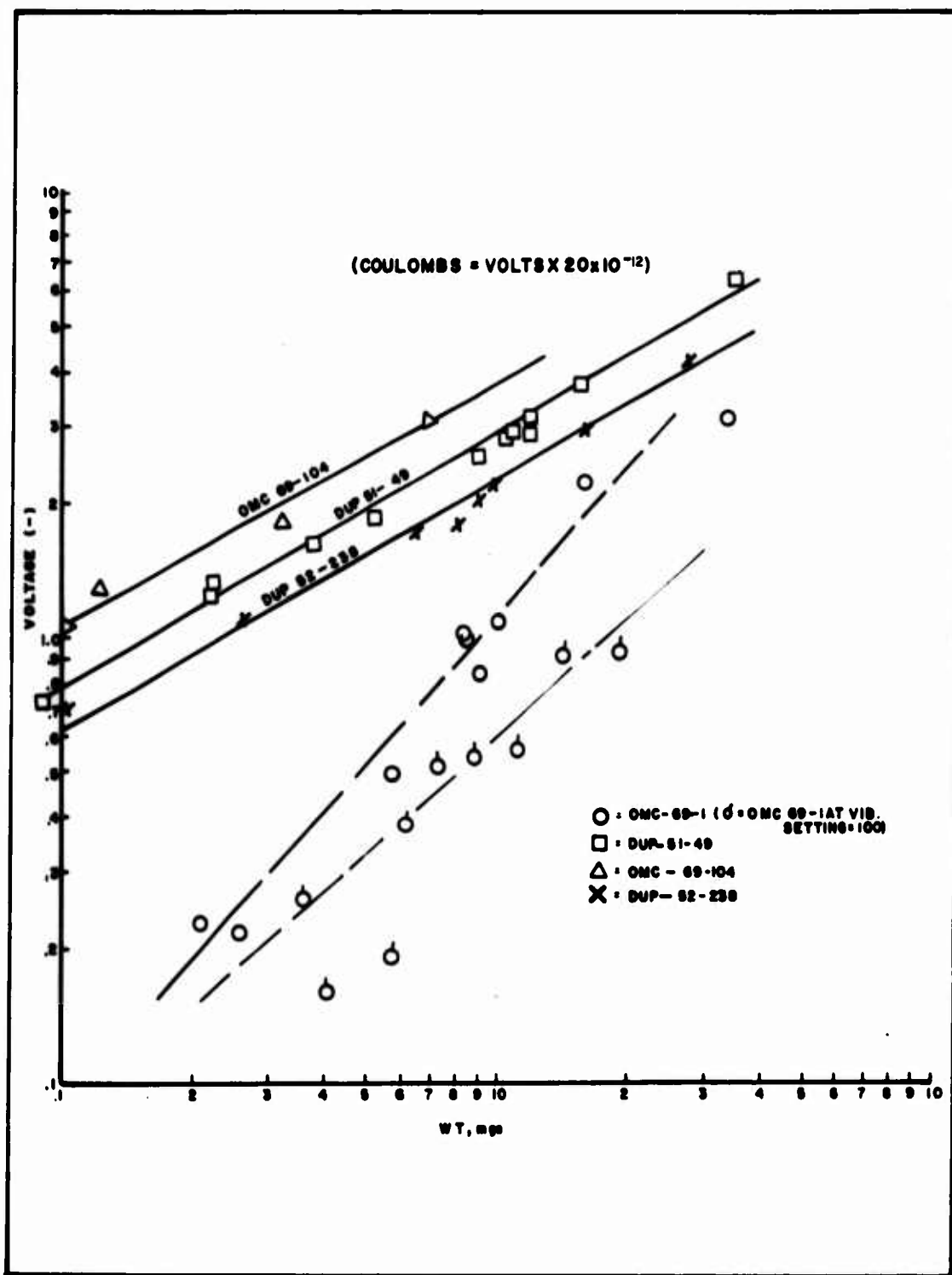
23

Fig 2   Vibrating trough apparatus

SYNTRON VIBRATORY
FEEDER AND POWER SUPPLY

TO ELECTRO-
METER

110 V 60N

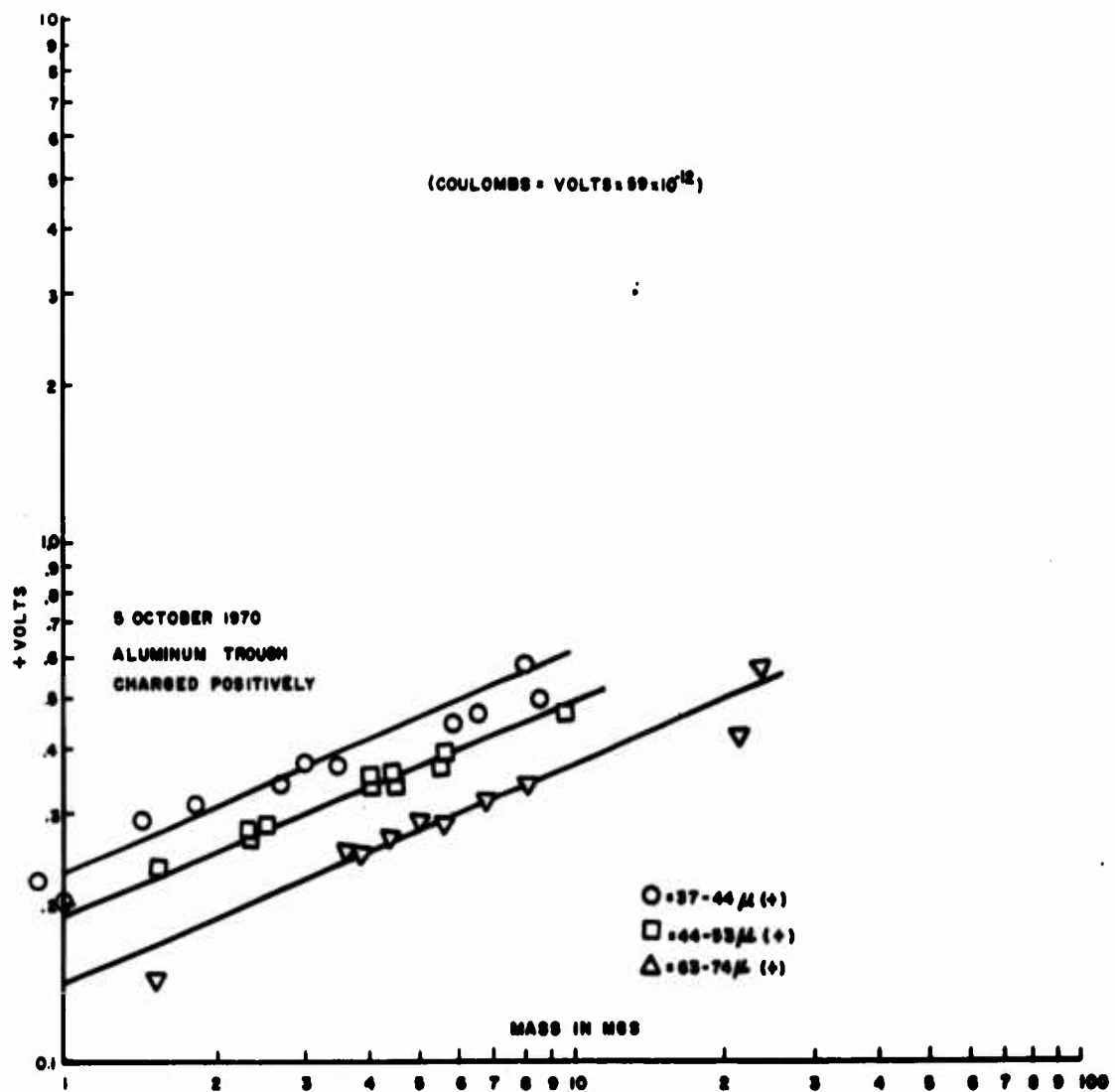Fig 3 Charge vs weight for different azide lots
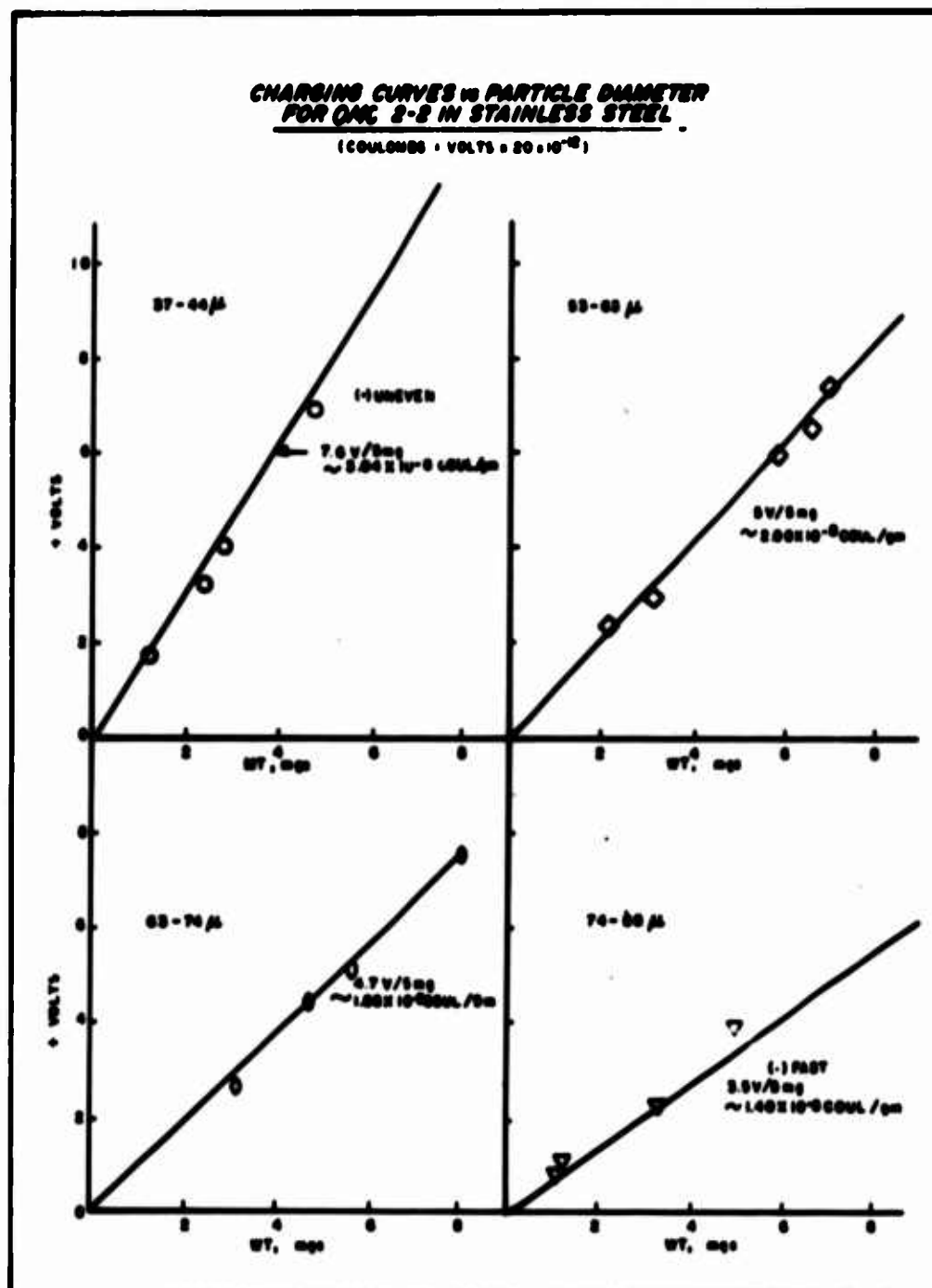
25

Fig 4   Effect of particle size on charging (Dup 51-49)

26

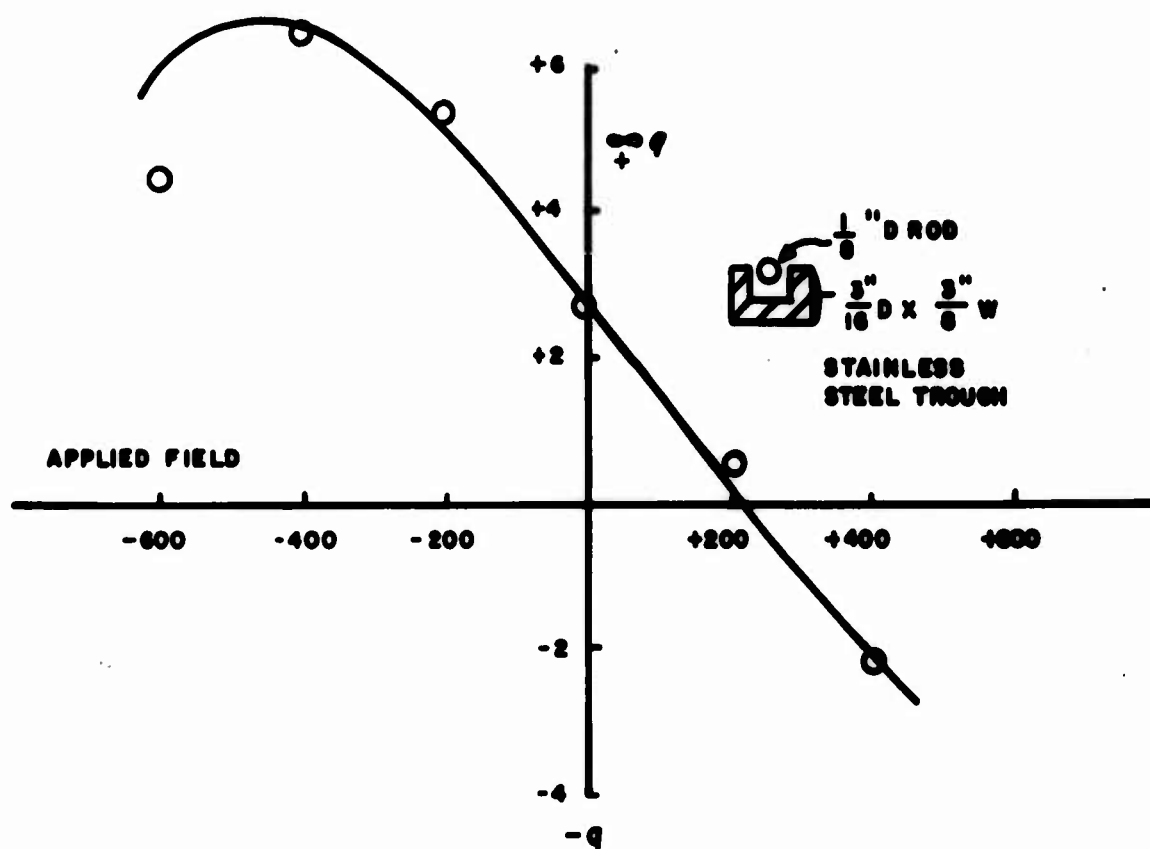**Fig 5   Charging curves vs particle diameter
for OMC 2-2 in stainless steel**

Fig 6   Charge on powder as function of applied voltage

28

APPENDIX A

Derivation of the Formula for Geometric Charge Densities on Particles

Let Q_i be the measured charge in coulombs of the ith size fraction

Let m_i be the sample weight in grams of the ith fraction

Let R_i be the arithmetic mean particle radius in cm. In this work, there is negligible difference between the geometric and arithmetic means because of the narrow range of the size fractions.

Let ρ be the effective density. Here, the effective density is the mass per unit volume of the sphere of radius R_i that "contains" a particle of radius R_i.

Let q_i be the surface charge density in coulombs/cm^2 on a particle of the ith size fraction.

Then,

$$q_i = Q_i/A_i$$

where A_i is the surface area of m_i grams of sample, and

$$A_i = \text{number of particles} \times \text{area per particle,}$$
$$= \frac{m_i}{4/3 \, \pi R^3 \, \rho} \quad \times 4 \, \pi R_i^2 = \frac{3m}{\rho \, R_i}$$

so that, substituting for A_i,

$$q_i = \frac{Q_i \, \rho \, R_i}{3m_i}$$

The data on charge density vs particle size in Table 4 were used to calculate charge densities according to Equation 2. In these calculations, the effective azide density was taken as e gm/cc, based on a crystal density of 4.7 gm/cc and visual estimate from the photomicrographs of Figures 1a-e.

29

APPENDIX B

Capacity of a Spherical Particle on a Metal Surface

The geometrical capacitance of a spherical particle near a metallic surface is given as (Ref 5, p 259):

$$C_{geom} = R(\Gamma + 1/2 \ln(2R/Z_c))$$

where C_{geom} is in esu; Γ, is Euler's constant, 0.5772; R is the particle radius in cm, and Z_c is the effective separation between the particle and the metal surface. The equation is valid for $Z_c \ll R$. Z_c is not well defined and may be a physical separation due to asperities or to a parameter involved in charge separation, such as the ratio of the thickness of a corrosion layer to its dielectric constant.

To estimate particle capacitances, it is sufficient to use an upper and a lower limit to the magnitude of Z_c in order to define a reasonable range of values, since C_{geom} will not be very sensitive to Z_c. For purposes of this estimate, Z_c is assumed to be represented by some physical features of the particle-metal system. The upper limit of the value of Z_c may be the height of asperities that define a physical separation. Such asperities may range from 0.1 to 1.0 microns (10^{-5} - 10^{-4} cm) in height. The lower limit to the value of Z_c may be in the range 1 - 10 Å, represented by the effective thickness of adsorbed gas or of reaction products. Thus a reasonable range of values would be 5 Å to 0.5 micron, or 5×10^{-8} to 5×10^{-5} cm. The value for 2R ranges from 37×10^{-4} to 89×10^{-4} in these experiments and is much greater than Z_c as required. Since the dependence on 2R is logarithmic in the bracketed term, no great error is introduced by taking the aritmetic mean diameter, 55×10^{-4}. Substituting and taking common logarithms gives:

$$C_{geom} = (2.9 \text{ to } 6.4)R$$

We will take C_{geom} = 4.5R, in esu, and conversion to farads gives C_{geom} = 0.5×10^{-11} R, or $1 - 2 \times 10^{-14}$ farads. It should be noted that the above calculation is for an isolated particle.

APPENDIX C

Induced Charging Due to an External Field

Assume that the particle is placed on one plate of a parallel two plate capacitor and that its charge due to contact potential in the absence of an external field is "q_0". In the presence of an applied field, E_o, the total charge will be:

$$Q = q_0 + AE_o$$

where A is related to an effective capacitance. If the particle radius is small in comparison to the electrode spacing, then E_o can be taken as the field at the plate holding the particle.
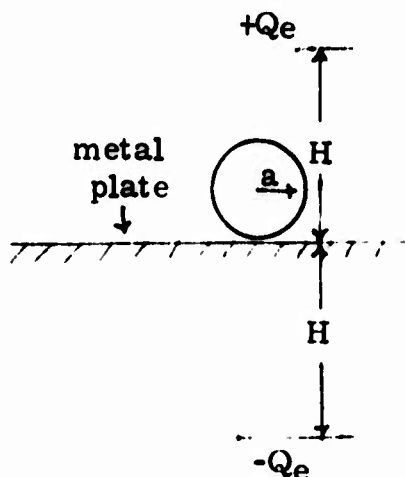
For a spherical particle the functional dependence on radius can be deduced by the method of images. Thus let E_o be replaced by two charges $+Q_e$ located at a distance $\pm H$ from the plane. Near the origin there is an approximately constant field, $E_o = 2Q_e/H^2$. With the sphere of radius "a" in place, image charges are induced equal to $+Q_e a/(H+a)$ and $-Q_e a/(H-a)$. The total charge on the sphere due to the inducing field is

$$Q = Q_e a(1/(H-a) - 1/(H+a))$$

$$= -2Q_e a^2/H^2 - a^2)$$

In the limit as $H \longrightarrow \infty$, and $Q_e \longrightarrow$ such that

$$\frac{2Q_e}{H^2} \longrightarrow E_o \text{ , } 2Q_e a^2/(H^2 - a^2)$$

$$\longrightarrow 2Q_e a^2/H^2 \quad a^2 E_o$$

$+Q_e$

metal plate

H

a

H

$-Q_e$

Thus for a spherical particle between plane parallel plates spaced at a distance L,

$$Q = q_o + a^2 V_{app}/L$$

The significant point of this calculation is the size dependence of the induced vis-a-vis the contact electrification. Thus in contact with a metal plate the particle acquires a spontaneous charge approximately proportional to its radius, and the charge due to an applied field is proportional to the square of the radius.